

Development of Hypercrosslinked Hydrophilic Polymer using Dispersion Polymerization Technique for Separation Process

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Abstract

Hypercrosslinked microsphere hydrophilic polymer derived from 2-hydroxyethyl methacrylate (HEMA), ethylene glycol dimethacrylate (EDGMA), and vinyl benzene chloride (VBC) have been successfully synthesized using hypercrosslinking reaction chemistry. In this study, dispersion polymerization technique has been used in order to develop precursor prior to hypercrosslinking reaction. Mixture of water/toluene system as a medium polymerization showed promising result with high yield and good quality of microsphere precursor and meanwhile increasing VBC content up to 5% based on monomer feed showed decreasing in quality of microsphere precursor in term of shape and size. FTIR result showed both EDGMA and VBC successfully incorporated into the precursor polymer backbone. After undergo hypercrosslinking reaction, hypercrosslinked microsphere polymer still can retain their original shape as before hypercrosslinking reaction with satisfy quality. From BET analysis, it showed slightly increment in specific surface area of hypercrosslinked microsphere polymer from 10.621 m²/g to 16.831 m²/g.

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1. INTRODUCTION

Rare earth elements (RRE) have been used extensively in human life. RRE consist the fifteen lanthanides plus scandium and yttrium and have been used in high tech application such as in wind turbine and fluorescent lamps (Schüler, Buchert, Liu, Dittrich, & Merz, 2011). Report shows that the demand for these elements is expected continuously to grow by more than 8% per year until 2020 (Commission, 2014). Approximately 95% of rare earths occur in only three minerals: monazite, xenotime, and bastnasite. Due to the chemical similarities, they are difficult to separate from each other (Gupta & Krishnamurthy, 1992). For the separation of rare earth elements, they are divided into the light rare earth and heavy rare earth. This classification is essential because basicity differences of the REE influence the solubilities of salts, the hydrolysis of ions, and the formation of complex species. These properties form the basis of separation procedures by fractional precipitation, ion exchange, and solvent extraction (Gupta & Krishnamurthy, 1992).

In solvent extraction method, the metal ion solution is mixed with an organic solvent. The presence of extractant chemicals in the organic phase improved the transfer of the metal ions into the organic phase. Eventhough this method have been widely used, it is still difficult to separate adjacent rare earth metals because such extractive separation processes are based on only the differences in the complex formation ability between the rare earth metals and their extractant (Nishihama, Hirai, & Komasaawa, 2003). Another major drawback of this method is that large amount of organic solvent is needed and not environmentally friendly (Gupta & Krishnamurthy, 1992).

In fractional precipitation method, the rare earths are stripped from loaded solvent extractants using aqueous solutions of inorganic acids. Then the dissolved rare earths will precipitate as insoluble carbonates and oxalates (Konishi & Noda, 2001). The major drawback of this method it needs further treatment to produce more valuable REE products (Kul, Topkaya, & Karakaya, 2008). Since the mid-20th century, ion exchange has been used to separate rare earth metals from each other and also from other metals (Gupta & Krishnamurthy, 1992). Because of the chemical similarities of the rare earth metals, complex agents are needed. Examples of these complex agents are α -hydroxyisobutyric acid (HIBA) and ethylenediaminetetraacetic acid (EDTA) (Pourjavid, Norouzi, Rashedi, & Ganjali, 2010).

All three conventional methods were designed to only recognize differences between ions on a single parameter. On the other hand chromatographic separations are designed to bind selectively with ions based on several parameters such as coordination chemistry and size, therefore it highly selective. As example, lanthanide can be separated using EDTA as a mobile phase (Fernández & García Alonso, 2008). Technology of molecular selectivity is well established and used widely in industries (Izatt, Izatt, & Bruening, 2010). Adsorbents for another rare earth ions such as Ce(III), La(III), and Cd(III) have already being synthesized (X.-Z. Li & Sun, 2007; Park & Tavlarides, 2010; Zhang et al., 2010). Meanwhile modified microporous hypercrosslinked polymers have been proven to be a good adsorbent for metal in chromatographic separations process (B. Li, Su, Luo, Liang, & Tan, 2011). The pore structure of hypercrosslinked polymer can be finely tuned and surface functionalities can be introduced by a wide variety of synthetic strategies. Therefore, because of these properties, hypercrosslinked polymer is also applicable to be used as adsorbent for rare earth metals.

Since 2004, a new method of hypercrosslinking reaction have emerged originating from the work of Davankov (Davankov, Ilyin, Tsyurupa, Timofeeva, & Dubrovina, 1996; Veverka & Jeřábek, 1999). The strategy of this method involved the development of precursor polymer particles using vinyl benzene chloride (VBC) to produce polymer particles with restricted level of crosslinking. Then this microsphere will be further crosslinked in a thermodynamically 'good' solvent such as dichloroethane (DCE). This reaction using FeCl_3 as the efficient lewis acid catalyst (Fontanals, Cortés, et al., 2005) will exploit the chloromethyl group as an 'internal' electrophile source (Fontanals, Manesiotis, Sherrington, & Cormack, 2008). These process involved conversion of chloromethyl group into methylene bridge; that formed pore after diluent were removed. The solvent which is DCE, has been used by Fontanals and co (Fontanals, Cormack, & Sherrington, 2008; Fontanals, Galià, et al., 2005; Fontanals, Marcé, Cormack, Sherrington, & Borrell, 2008; Fontanals et al., 2014) to produce hypercrosslinked microsphere in the range of 800 to 1500 $\text{m}^2 \text{g}^{-1}$.

Since 1960, polyHEMA has been developed as hydrogel and spark interest in development of these molecules (Wichterle & Lim, 1960). PolyHEMA is a non-toxic polymer contrast to the toxic polymer of HEMA monomer. Cytotoxicity test proved that polyHEMA is a non-toxic to living cells (Zecheru, Salageanu, Cincu, Chappard, & Zerroukhi, 2008). PolyHEMA capable to swell in water or biological fluids and retain a large amount of fluids in the swollen state (Nicolson & Vogt, 2001). This happened because of the presence of several hydrophilic inside polyHEMA molecules such as $-\text{COO}-$ and $-\text{OH}$ (Hoffman, 2012).

Because of the capabilities of molecules to retain water content inside, it can affect different properties like surface properties, mechanical properties, permeability and biocompatibility. PolyHEMA also permit molecules of different size to diffuse in or out inside it, thus such polymer is very useful in application such as a drug delivery system (Tomar, Tomar, Gulati, & Nagaich, 2012). Other than drug delivery application, these unique capabilities also allowed polyHEMA to be used as ion-exchange resin for metal separation or in other separation application. Apart from that, major advantages of using polymer beads as strong anion resin are enhanced mechanical stability, improve process ability and durability (Green, Grubjesic, Lee, & Firestone, 2009; Yuan & Antonietti, 2011).

This paper discussed about the development of hydrophilic polymer precursor derived from both hydrophilic molecules; HEMA and EDGMA with incorporate with VBC and its subsequent reaction in hypercrosslinked chemistry. This microsphere then will be served as alternative routes for metal separation.

2. MATERIAL AND METHODS

2.1. Reagents and Standards

2-hydroethylmethacrylate (HEMA) 97% contains 200 ppm monomethyl ether hydroquinone, ethylene glycol dimethacrylate (EDGMA) contains 90-110 ppm of monomethyl ether hydroquinone, 4-vinylbenzyl chloride (VBC), 97%, polyvinylpyrrolidone (PVP), and benzoyl peroxide obtained from Sigma Aldrich while toluene was obtained from HmbG Chemical. All chemicals except HEMA, EDGMA and benzoyl peroxide were used without purification. HEMA, EDGMA and benzoyl peroxide were purified prior to synthesis. The reagents that used in the hypercrosslinked reaction were 1,2-Dichloroethane 99.0 % from Sigma Aldrich and Iron (III) Chloride from HmbG Chemicals.

2.2. Precursor Synthesis

Microbeads precursor was prepared using modified dispersion polymerization. Dispersion medium was prepared by dissolving PVP within 50 mL of distilled water. 12 mL of toluene then mixed with HEMA, PVP then benzoyl peroxide before being stirred until homogeneous. The mixture then being transferred into the dispersion medium placed in mechanical stirred at constant rate of 300 rpm. After one hour, EDGMA and VBC were added to the mixture. The reactor was flushed by nitrogen during the experiment. Polymerization process was conducted at 65 °C for 4 hours and 90 °C for 2 hours. After polymerization, the microsphere then was being washed by distilled water and ethyl alcohol before dry in vacuum for 24 hours (Kesenci, Tuncel, & Pişkin, 1996).

2.3. Hypercrosslinked Reaction

1.5 g of microsphere precursor was added into 40 mL of 1,2-Dichloroethane (DCE) . The reaction was left under nitrogen for one hour at room temperature. Ferum (III) chloride was added and mixture heated at 80 °C for 18 hours. Hypercrosslinked particles then recovered, washed with methanol and acid nitric before settled in soxhlet extractor with acetone overnight. The particles then washed again with methanol and diethyl ether before being left dried in oven at 40 °C oven for overnight (Fontanals, et al., 2014).

2.4. Particles Characterization

The surface structure and morphology of the precursor polymer and hypercrosslinked particle was captured by using Scanning Electron Microscopy (SEM) UNIT JOEL.JSM- 7800F model. The analysis was carried out at a condition of 20X, 30X, and 60X. Brunauer-Emmet-Teller (BET) analysis was carried out using Thermo-Scientific to determine the specific surface area of the hypercrosslinked polymer. In the analysis, liquid N₂ used as an adsorbate at temperature 77K. Fourier transform infrared spectroscopy (FTIR) used to obtain an infrared spectrum of functional group were supplied by Universiti Malaysia Pahang.

3. RESULTS AND DISCUSSION

3.1. Synthesis of Precursor


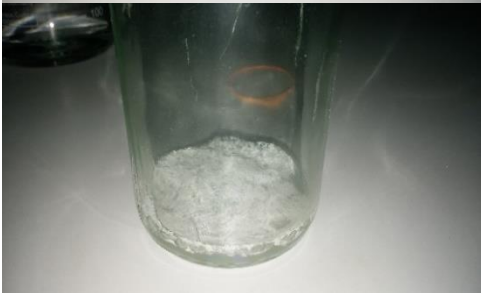
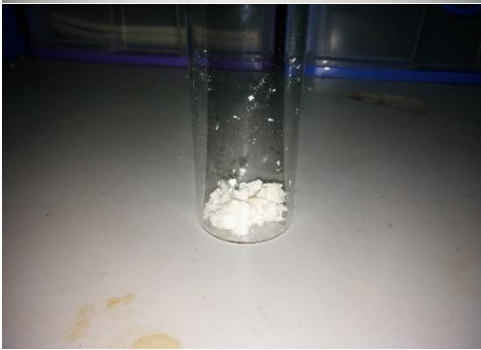
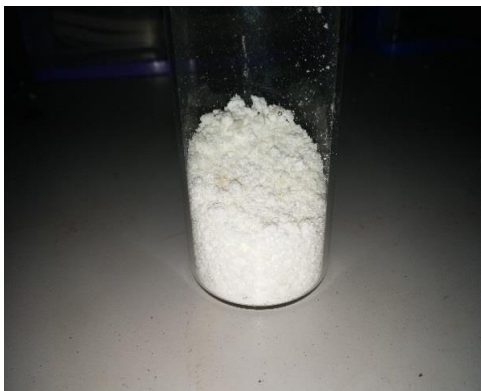
3.1.1. Effect of solvent mixture on precursor

In this study, four solvents mixtures systems were used which were ethanol/water, 2-butanol/water, acetonitrile/water, and toluene/water. All the solvents were mixed with distilled water with the ratio of 20:80. All other parameters were fixed. The results are shown in Table 1.

From the Table 1, the particles in both ethanol/water and 2-butanol/water solvents mixtures were producing gel like structures after reaction finished and become solid when dried in vacuum oven for overnight. In case of 2-butanol/water system, products become harden at a shorter time

compare to ethanol/water products. No yield was obtained for both of ethanol/water and 2-butanol/water solvents systems. For acetonitrile/water and toluene/water solvents system, both systems were producing solid particles at the end of reaction time but in toluene/water system, it shows promising results which beads formed with good quality compare to acetonitrile/water system. Also, yield obtained in toluene/water system higher than acetonitrile/water system which 86.71% and 11.9% yield respectively

Table 1: Effects of solvent systems on the production of poly(HEMA-co-VBC-co-EDGMA) with fixed EGDMA, HEMA, and VBC amount.

Solvent	Physical Features	Remarks
Ethanol/ Water		<ul style="list-style-type: none"> • Solid gel • No beads formed • Yield: N/A
2-butanol/ Water		<ul style="list-style-type: none"> • Solid gel • No beads formed • Yield: N/A
Acetonitrile/ Water		<ul style="list-style-type: none"> • Agglomerate solid • No individual beads formed • Yield: 11.9%
Toluene/ Water		<ul style="list-style-type: none"> • Spherical solid • Individual beads formed • Yield: 86.71%

3.1.2. Effect of VBC amount

VBC as co-monomer also can give a significant effect to the final products. Increasing VBC content to 5% give effect to the shape of the microspheres as shown in Figure 1.

As showed in Figure 1, well-defined spherical shape can be observed when no VBC were incorporated into the microspheres. Individual beads can be easily been identified in both pictures. However in 5% of VBC content showed more agglomerated microspheres compared to no VBC content added to the reaction. Both microspheres obtained from 0% VBC content and 5% VBC content have size range between 100-450 μm . The particle size distribution both microspheres can be seen in Figure 2.

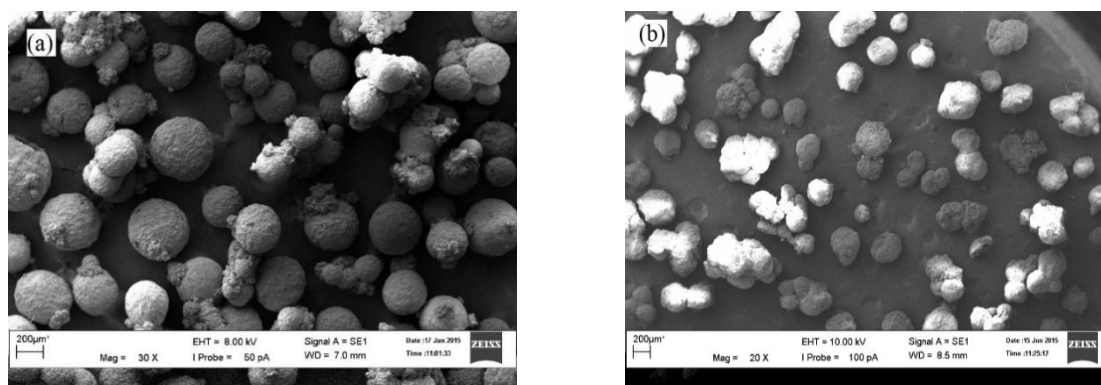


Figure 1: SEM result of two set of microspheres with different VBC content a) 0% VBC and b) 5% VBC

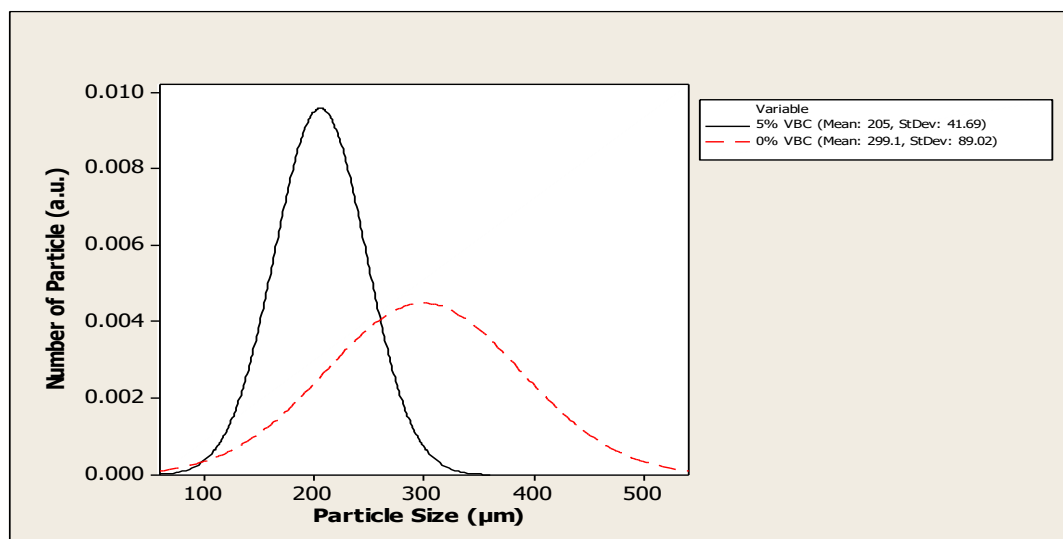


Figure 2: Particle size distribution of microspheres with 0% and 5% of VBC content

Figure 2 showed particles size distribution of microspheres with 0% and 5% VBC content. Standard deviation of 5% VBC microspheres was smaller than microspheres with no VBC content with standard deviation of 41.69 and 89.02 respectively. While, 0% of VBC microspheres have larger size compared to 5% of VBC microspheres based on the mean value. However both result showed highly polydispersed in the term of size. The polydispersity of products could be attributed to the presence of two/three different co-monomers during polymerization process (Bratkowska et al, 2010).

3.1.3. FTIR Result for precursor microspheres

The FTIR result of poly(HEMA-co-EDGMA-co-VBC) are shown in Figure 3. A broad peak at the region 3500 cm^{-1} shows characteristic of hydroxyl group inside polyHEMA (Kesenci, et al., 1996; Kumar, Ganapathy, Kim, Jeong, & Jeong, 2008; Soykan, Delibas, & Coskun, 2007). Another important functional group inside polyHEMA is ester group. A sharp peak at 1740 cm^{-1} shows the existence of ester group inside the particles (Soykan, et al., 2007). Therefore it proves the existence of HEMA incorporated into the polymer chains. A sharp peak of 1740 cm^{-1} also contributed from ester functional group in EDGMA (Tuncel & Pişkin, 1996). Peak at 1265 cm^{-1} region showed the existence of chlorine (C-Cl) stretch inside the particle which it contributed from VBC.

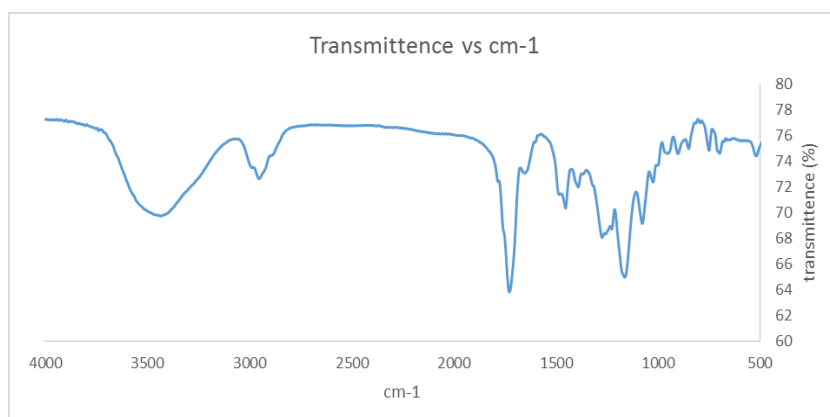


Figure 3: FTIR spectra for precursor poly(HEMA-co-EDGMA-co-VBC) microsphere

3.2. Synthesis of Precursor

3.2.1. Morphology of hypercrosslinked polymer

After undergo hypercrosslinking reaction, hypercrosslinked microsphere polymer still can retain their original shape before hypercrosslinking reaction with satisfy quality. The SEM images of hypercrosslinked polymer beads can be seen in Figure 4.

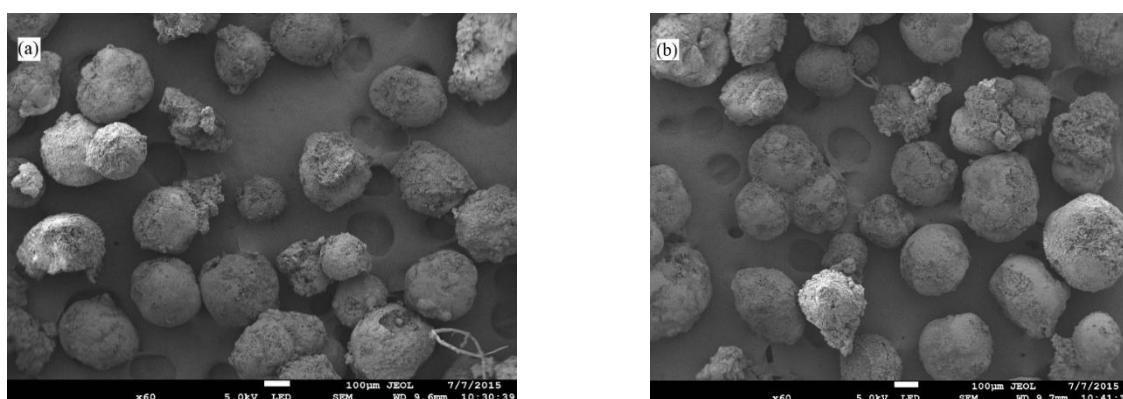


Figure 4: SEM images of hypercrosslinked polymer beads after undergo hypercrosslinking reaction for a) 4 hours and b) 18 hours

From Figure 4, the shape of hypercrosslinked polymer beads was almost identical to the shape of precursor even after undergo 18 hours of reaction time in DCE. The retain shape could be attributed to the presence of high content of crosslinker (40% relative to monomer feed in precursor). This crosslinker give extra rigidity to the microsphere.

3.2.2. FTIR Result for hypercrosslinked polymer

However, extra rigidity can give problem in hypercrosslinking reaction. This extra unnecessary rigidity makes the microspheres harder to swell when it left in DCE. Therefore, it can prevent chlorine atoms to diffuse in and out from inside the microspheres. From Figure 5, the spectra of hypercrosslinked polymer beads does not differed to much with precursor microspheres spectra. The chlorine peak does not show any reduction in intensity even after hypercrosslinking reaction; showed that conversion of chlorine to methylene bridge did not occurred. This might be due to the presence of small amount of chlorine from VBC. Surprising, BET analysis showed slightly increasing in value of specific surface area from 10.621 m²/g before hypercrosslinking reaction to 16.831 m²/g after hypercrosslinking reaction. Therefore, it showed that conversion of chlorine into the methylene bridge was still occurred during hypercrosslinking reaction

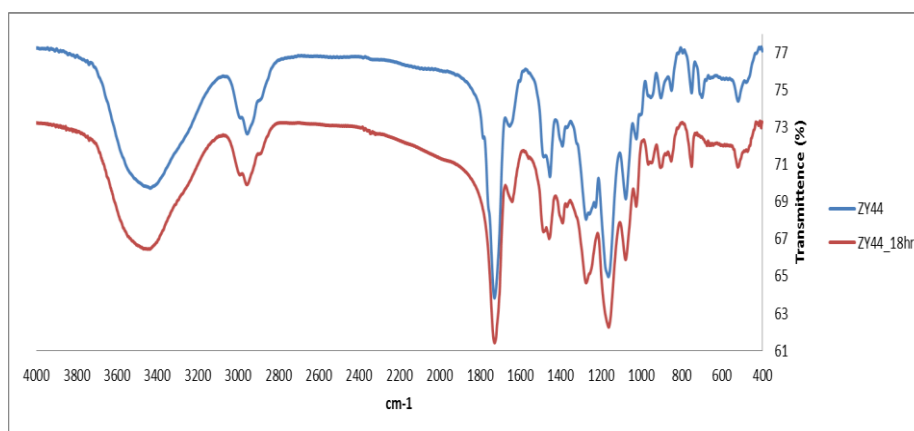


Figure 5: FTIR spectra for hypercrosslinked polymer (red) and precursor microsphere (blue)

4. CONCLUSION

For the synthesis of poly(HEMA-co-EDGMA-co-VBC) precursor, the best solvent system is a mixture of toluene and water. Using the mixture solvent system, solid particle beads successful obtained with very high yield. The quality of the microspheres reduced when second monomer introduced to the system. Odd shaped was more prominent in 5% of VBC compared to 0% of VBC. FTIR result of precursor showed all the functional group has been successfully incorporated into the polymer backbone. A broad peak at the region 3500 cm⁻¹ showed the characteristic of hydroxyl group, a sharp peak at 1740 cm⁻¹ showed the characteristic of ester group and peak at 1265 cm⁻¹ showed the characteristic of chlorine atoms. High amount of crosslinker provide rigidity to microspheres to retain their shape during hypercrosslinking reaction. However the extra rigidity prevents microspheres to swell well thus causes less conversion of chloromethyl group to methylene bridges. Eventhough FTIR result for hypercrosslinked polymer beads showed no significant reduction in chloromethyl functional group; however the increasing of specific surface area from 10.621 m²/g to 16.831 m²/g showed that slightly conversion of chloromethyl to methylene bridges still occurred. This studied showed that hydrophilic polymer beads have potential as adsorbent in separation process. Further study will be conducted to modify the hypercrosslinked to suit with particular separation process.

REFERENCES

Bratkowska, D., Fontanals, N., Borrull, F., Cormack, P. A. G., Sherrington, D. C., & Marcé, R. M. (2010). Hydrophilic hypercrosslinked polymeric sorbents for the solid-phase extraction of polar contaminants from water. *Journal of Chromatography A*, 1217(19), 3238-3243.

- Commission, E. (2014). Report of the Ad-hoc Working Group on defining critical raw materials. Brussels.
- Davankov, V., Ilyin, M., Tsyurupa, M., Timofeeva, G., & Dubrovina, L. (1996). From a dissolved polystyrene coil to an intramolecularly-hyper-cross-linked "Nanosponge". *Macromolecules*, 29(26), 8398-8403.
- Fernández, R. G., & García Alonso, J. I. (2008). Separation of rare earth elements by anion-exchange chromatography using ethylenediaminetetraacetic acid as mobile phase. *Journal of Chromatography A*, 1180(1-2), 59-65.
- Fontanals, N., Cormack, P. A., & Sherrington, D. C. (2008). Hypercrosslinked polymer microspheres with weak anion-exchange character: Preparation of the microspheres and their applications in pH-tunable, selective extractions of analytes from complex environmental samples. *Journal of Chromatography A*, 1215(1), 21-29.
- Fontanals, N., Cortés, J., Galià, M., Maria Marcé, R., Cormack, P. A. G., Borrull, F., et al. (2005). Synthesis of Davankov-type hypercrosslinked resins using different isomer compositions of vinylbenzyl chloride monomer, and application in the solid-phase extraction of polar compounds. *Journal of Polymer Science Part A: Polymer Chemistry*, 43(8), 1718-1728.
- Fontanals, N., Galià, M., Cormack, P. A., Marcé, R. M., Sherrington, D. C., & Borrull, F. (2005). Evaluation of a new hypercrosslinked polymer as a sorbent for solid-phase extraction of polar compounds. *Journal of Chromatography A*, 1075(1), 51-56.
- Fontanals, N., Manesiotis, P., Sherrington, D. C., & Cormack, P. A. G. (2008). Synthesis of Spherical Ultra-High-Surface-Area Monodisperse Amphipathic Polymer Sponges in the Low-Micrometer Size Range. *Advanced Materials*, 20(7), 1298-1302.
- Fontanals, N., Marcé, R. M., Cormack, P. A., Sherrington, D. C., & Borrull, F. (2008). Monodisperse, hypercrosslinked polymer microspheres as tailor-made sorbents for highly efficient solid-phase extractions of polar pollutants from water samples. *Journal of Chromatography A*, 1191(1), 118-124.
- Fontanals, N., Miralles, N., Abdullah, N., Davies, A., Gilart, N., & Cormack, P. (2014). Evaluation of strong cation-exchange polymers for the determination of drugs by solid-phase extraction-liquid chromatography-tandem mass spectrometry. *Journal of Chromatography A*, 1343, 55-62.
- Green, O., Grubjesic, S., Lee, S., & Firestone, M. A. (2009). The design of polymeric ionic liquids for the preparation of functional materials. *Polymer Reviews*, 49(4), 339-360.
- Gupta, C., & Krishnamurthy, N. (1992). Extractive metallurgy of rare earths. *International Materials Reviews*, 37(1), 197-248.
- Hoffman, A. S. (2012). Hydrogels for biomedical applications. *Advanced drug delivery reviews*, 64, 18-23.
- Izatt, S. R., Izatt, N. E., & Bruening, R. L. (2010). Metal separations of interest to the Chinese metallurgical industry. *Journal of Rare Earths*, 28, Supplement 1, 22-29.
- Kesenci, K., Tuncel, A., & Pişkin, E. (1996). Swellable ethylene glycol dimethacrylate-hydroxyethylmethacrylate copolymer beads. *Reactive and Functional Polymers*, 31(2), 137-147.
- Konishi, Y., & Noda, Y. (2001). Precipitation Stripping of Rare-Earth Carbonate Powders from Rare-Earth-Loaded Carboxylate Solutions Using Carbon Dioxide and Water. *Industrial & Engineering Chemistry Research*, 40(8), 1793-1797.
- Kul, M., Topkaya, Y., & Karakaya, İ. (2008). Rare earth double sulfates from pre-concentrated bastnasite. *Hydrometallurgy*, 93(3-4), 129-135.
- Kumar, N. A., Ganapathy, H. S., Kim, J. S., Jeong, Y. S., & Jeong, Y. T. (2008). Preparation of poly 2-hydroxyethyl methacrylate functionalized carbon nanotubes as novel biomaterial nanocomposites. *European Polymer Journal*, 44(3), 579-586.
- Li, B., Su, F., Luo, H.-K., Liang, L., & Tan, B. (2011). Hypercrosslinked microporous polymer networks for effective removal of toxic metal ions from water. *Microporous and Mesoporous Materials*, 138(1), 207-214.

- Li, X.-Z., & Sun, Y.-P. (2007). Evaluation of ionic imprinted polymers by electrochemical recognition of rare earth ions. *Hydrometallurgy*, 87(1), 63-71.
- Nicolson, P. C., & Vogt, J. (2001). Soft contact lens polymers: an evolution. *Biomaterials*, 22(24), 3273-3283.
- Nishihama, S., Hirai, T., & Komasaawa, I. (2003). Advanced liquid-liquid extraction systems for the separation of rare earth ions by combination of conversion of the metal species with chemical reaction. *Journal of Solid State Chemistry*, 171(1-2), 101-108.
- Park, H.-J., & Tavlarides, L. L. (2010). Adsorption of neodymium (III) from aqueous solutions using a phosphorus functionalized adsorbent. *Industrial & Engineering Chemistry Research*, 49(24), 12567-12575.
- Pourjavid, M., Norouzi, P., Rashedi, H., & Ganjali, M. (2010). Separation and direct detection of heavy lanthanides using new ion-exchange chromatography: fast Fourier transform continuous cyclic voltammetry system. *Journal of Applied Electrochemistry*, 40(9), 1593-1603.
- Schüler, D., Buchert, M., Liu, R., Dittrich, S., & Merz, C. (2011). Study on rare earths and their recycling. *Öko-Institut eV Darmstadt*.
- Soykan, C., Delibas, A., & Coskun, R. (2007). Copolymers of N-(4-bromophenyl)-2-methacrylamide with 2-hydroxyethyl methacrylate. *EXPRESS POLYMER LETTERS*, 1(9), 594-603.
- Tomar, N., Tomar, M., Gulati, N., & Nagaich, U. (2012). pHEMA hydrogels: Devices for ocular drug delivery. *International Journal of Health & Allied Sciences*, 1(4), 224.
- Tuncel, A., & Pişkin, E. (1996). Nonswellable and swellable poly(EGDMA) microspheres. *Journal of applied polymer science*, 62(5), 789-798.
- Veverka, P., & Jeřábek, K. (1999). Mechanism of hypercrosslinking of chloromethylated styrene-divinylbenzene copolymers. *Reactive and Functional Polymers*, 41(1-3), 21-25.
- Wichterle, O., & Lim, D. (1960). Hydrophilic gels for biological use.
- Yuan, J., & Antonietti, M. (2011). Poly (ionic liquid) latexes prepared by dispersion polymerization of ionic liquid monomers. *Macromolecules*, 44(4), 744-750.
- Zecheru, T., Salageanu, A., Cincu, C., Chappard, D., & Zerroukhi, A. (2008). Poly (HEMA-co-MOEP) microparticles:optimisation of the preparation method and in vitro tests *U.P.B. Sci. Bull., Series B*, 70(1), 3.
- Zhang, X., Li, C., Yan, Y., Pan, J., Xu, P., & Zhao, X. (2010). A Ce³⁺-imprinted functionalized potassium tetratitanate whisker sorbent prepared by surface molecularly imprinting technique for selective separation and determination of Ce³⁺. *Microchimica Acta*, 169(3-4), 289-296.